Hyperfine spectra of CH$_3$F nuclear spin conversion

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Abstract

A theoretical model of hyperfine spectra of nuclear spin conversion of molecular isomers has been developed. The model takes into account the nuclear spin-spin and spin-rotation interactions, as well as the saturation of intramolecular mixing of molecular ortho and para states. The model has been applied to hyperfine spectra of nuclear spin conversion in ^{13}CH$_3$F molecules subjected to an external electric field. Conditions under which the hyperfine structure in the spectra can be resolved have been determined.

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I. INTRODUCTION

Recently, much attention has been devoted to the investigation of the level-crossing resonances in the spin isomer conversion (*conversion spectra*) in CH_3F [1–7]. The goal was to test the mechanism of the ortho-para conversion in this molecule. The importance of these efforts is clear. CH_3F is the first and until now the only polyatomic molecule in which a spin conversion mechanism was identified. On the other hand, one may expect a similar conversion mechanism in other symmetrical molecules too.

The essence of the isomer conversion spectra consists of the following. An external homogeneous electric field splits the molecular states. At some electric field the ortho and para states of the molecule cross which, speeds up the rate of conversion. Scanning of the electric field gives the field dependence of conversion rate which is the conversion spectrum. Measurements of the conversion spectra are presently performed at room temperature.

The usefulness of the conversion spectra should not be limited to the investigation of the conversion itself. In fact, this is a new physical effect which can find various applications. For example, it was proposed [3] to measure with the help of the conversion spectra characteristics of molecular spin-rotation interaction which are hardly accessible by ordinary methods. Many of these applications require a deeper understanding of the phenomenon. Up to now, only the rotational structure in the conversion spectra resulting from M-splitting of molecular states has been considered. This is sufficient for the conversion spectra of ~ 1 MHz resolution. Higher resolution needs an account of the hyperfine structures in the conversion spectra, which has not been done before. In this paper we perform such an analysis and determine the conditions at which these hyperfine structures can be observed. We check also an accuracy of the simplified approach to the conversion spectra in which hyperfine splitting of molecular states is neglected. The calculations are done for $^{13}CH_3F$ because for this molecule the rotational structure in the conversion spectra was experimentally observed recently [5]. The spectral resolution achieved already in [5] was better than 6 MHz. It makes the $^{13}CH_3F$ molecule the best candidate for the observation of the hyperfine structures in the conversion spectra.

II. QUANTUM RELAXATION OF SPIN ISOMERS

Ordinary gaseous relaxation processes are insensitive to a tiny hyperfine splitting of molecular states. This is a consequence of the fact that the kinetic energy of colliding particles is much larger than the hyperfine level splitting. For the nuclear spin conversion in molecules the situation can be different if the conversion is induced by intramolecular state mixing and collisional interruption of this mixing (we will refer to this process as *quantum relaxation* [8]) which is rather sensitive to the ortho-para level splitting.

The CH_3F molecules exist in the form of two nuclear spin isomers [9]. The total spin of the three hydrogen nuclei in the molecule can have the magnitude either $I = 3/2$ (ortho isomers), or $I = 1/2$ (para isomers). Angular momentum projections (K) on the molecular symmetry axis divisible by 3 are allowed only for ortho isomers. For para isomers all other K values are allowed. Consequently, the quantum states of the CH_3F molecule are divided into

two subspaces which are schematically shown in Fig. 1. Qualitatively, CH$_3$F spin conversion by quantum relaxation can be described as follows. Suppose that at the beginning of the process a test molecule is placed into the ortho subspace. Due to collisions with surrounding gas particles, which cannot change the spin state of the molecule, the test molecule starts to perform fast migration along rotational states inside the ortho subspace. This running up and down along the ladder of the ortho states continues until the molecule jumps into the state m which is mixed by an *intramolecular* perturbation $\hat{V}$ with the energetically close para state n. During the free flight after this collision, para state n will be admixed with the ortho state m. Consequently, the next collision can transfer the molecule into other para states and thus localize it inside the para subspace. More details on quantum relaxation of nuclear spin isomers can be found in Refs. [10–12].

Quantum relaxation of nuclear spin isomers of molecules can be quantitatively described in the framework of the density matrix formalism. The result of this description is the following [12]. One has to divide the molecular Hamiltonian into two parts

$$\hat{H} = \hat{H}_0 + \hat{V}, \tag{1}$$

where the main part of the Hamiltonian, $\hat{H}_0$, has pure ortho and para states as the eigenstates, and $\hat{V}$ is a small perturbation which mixes the ortho and para states. In the Ref. [12] the hyperfine contribution to the term $\hat{H}_0$ was neglected and it was assumed that the molecule is not subjected to an external field.

Suppose that at the instant $t = 0$ a nonequilibrium concentration of, e.g., ortho molecules, $\delta\rho_o(0)$, was created. the solution of the problem gives an exponential isomer conversion: $\delta\rho_o(t) = \delta\rho_o(0)e^{-\gamma t}$, with the rate

$$\gamma = \sum_{\alpha \in o, \alpha' \in p} \frac{2\Gamma \mid V_{\alpha\alpha'} \mid^2}{\Gamma^2 + \omega_{\alpha\alpha'}^2}(W_\alpha + W_{\alpha'}). \tag{2}$$

Here Γ is the collisional decay rate of the off-diagonal density matrix elements,

$$(\partial\rho_{\alpha\alpha'}/\partial t)_{coll} = -\Gamma\rho_{\alpha\alpha'}; \quad \alpha \in ortho, \ \alpha' \in para, \tag{3}$$

assumed to be the same for all ortho-para level pairs; $\omega_{\alpha\alpha'}$ is the gap between the states $|\alpha >$ and $|\alpha' >$; W_α and $W_{\alpha'}$ are the Boltzmann factors. Solution (2) was obtained under the assumption that collisions do not transfer molecules directly from ortho to para states, i.e., the cross-section $\sigma(ortho|para) = 0$. The validity of this assumption has been discussed in detail in the review [13].

At low gas pressure, when $\Gamma \ll \omega$, the conversion rate is proportional to Γ, thus being *proportional* to the gas pressure. In this limiting case, the pressure dependence of the conversion rate is quite similar to ordinary gaseous relaxation which is linear in pressure too. On the other hand, in this pressure limit the conversion rate is sensitive to the ortho-para level splitting (note ω in the denominator of (2)) thus having a distinctive signature, unusual for gaseous relaxation processes. This strong dependence on ω is at the heart of the level-crossing effect at the spin isomer conversion.

III. STARK LEVEL SPLITTING

Calculation of the ortho-para state mixing is rather complicated, especially if one has to account for both the Stark and hyperfine level splitting. In this case special care should be taken about proper symmetrization of states and their transformation under these perturbations. Let us consider first the quantum states of the free molecule and ignore the hyperfine perturbation. Spin-rotational states in the ground electronic and vibrational state of CH_3F can be constructed as follows [14,15]. To determine the molecular position in space, one introduces a system of coordinates (xyz) fixed in the molecule (Fig. 2). By combining rotational and nuclear spin states, one introduces the states $|\beta>$ which are invariant under cyclic permutation of the three hydrogen nuclei

$$|\beta> \equiv |J,K,M>|I,\sigma,K>; \quad |\overline{\beta}> \equiv |J,-K,M>|I,\sigma,-K>; \quad K \geq 0, \qquad (4)$$

where $|J,K,M>$ are the quantum states of symmetric top characterized by the angular momentum (J), its projection (K) on the z axis of the molecular system of coordinates and the angular momentum projection (M) on the quantization Z axis of the laboratory system of coordinates. I and σ are the total spin of the three hydrogen nuclei and its projection on the Z axis, respectively. The explicit expressions for the spin states $|I,\sigma,K>$ are given in [14]. These expressions specify the allowed K-quantum numbers for the ortho and para spin isomers as was explained in Section II.

Permutation of any two hydrogen nuclei in CH_3F inverts the z axis of the molecular system of coordinates. Such permutations, e.g., the permutation P_{23}, acts on the state $|\beta>$ as $P_{23}|\beta> = (-1)^J|\overline{\beta}>$. Because the states $|\beta>$ are invariant under cyclic permutation of the three hydrogen nuclei, a similar result is valid for the other two permutations of hydrogen pairs: P_{12} and P_{31}.

States $|\beta>$ and $|\overline{\beta}>$ generate a two-dimensional representation of the molecular symmetry group. Spin-rotation states, which generate one-dimensional representations are

$$|\beta,\kappa> \equiv \frac{1}{\sqrt{2}}\left[(-1)^\kappa + P_{23}\right]|\beta>; \quad \kappa = 0,1. \qquad (5)$$

From this definition it is easy to conclude that the symmetry of states $|\beta,\kappa>$ is determined by the rule: $P_{23}|\beta,\kappa> = (-1)^\kappa|\beta,\kappa>$ and by similar relations for the permutations of the other two pairs of protons.

Further, one has to take into account the molecular inversion states. Let us designate the antisymmetric and symmetric inversion states of the molecule as $|s=0>$ and $|s=1>$, respectively. Permutation of two protons, e.g., P_{23}, acts on the inversion states as [15]

$$P_{23}|s=0> = -|s=0>; \quad P_{23}|s=1> = |s=1>. \qquad (6)$$

The total quantum states of CH_3F have to be antisymmetric under the permutation of any two hydrogen nuclei because protons are fermions. Consequently, the only allowed molecular states are $|\beta,\kappa=s>|s>$.

The last step is to account for the spin states of the fluorine and carbon (^{13}C) nuclei, both having spin $1/2$. Finally, the molecular states are

$$|\alpha_s> \equiv |\beta, \kappa = s> |s> |\sigma^F> |\sigma^C>,$$ (7)

where σ^F and σ^C denote, respectively, the projections of the fluorine and carbon nuclear spins on the laboratory quantization Z axis. The states (7) of the free molecule will be denoted as the α-basis. For rigid symmetric tops, like CH$_3$F is, the states $|\alpha_s>$ are degenerate in the quantum numbers M, σ, σ^F, σ^C and s.

An external electric field due to the Stark perturbation, $\hat{V}_{St} = -\mathbf{d}\mathcal{E}$, mixes the states having $|\Delta s| = 1$ and $|\Delta J| \leq 1$. In the following, we will consider relatively weak electric fields which produce Stark splitting much smaller than the J-splitting. Consequently, the Stark mixing of states having $|\Delta J| = 1$ can be neglected and one has to solve the Schrödinger equation for the doubly degenerate states $|\alpha_0>$; $|\alpha_1>$. In a standard way [9], one can find the energy of the new states,

$$E(\beta, \xi) = E_{free}(J, K) + (-1)^\xi \frac{K|M|}{J(J+1)} d\mathcal{E}; \quad \xi = 0, 1,$$ (8)

where $E_{free}(J, K)$ is the energy of a free molecule; d is the so-called permanent electric dipole moment of the molecule; $\mathcal{E}$ is the electric field strength; ξ is the quantum number of the new molecular states which are

$$|\beta, \xi> = \frac{1}{2} \left[(-1)^\xi \frac{M}{|M|} |s = 0> (1 + P_{23}) + |s = 1> (1 - P_{23}) \right] |\beta>.$$ (9)

The magnitude of the electric dipole moment, d, is determined by the molecular spatial and electronic structure [14]

Similar to the case of a free molecule, one has to take into account the spin states of fluorine $|\sigma^F>$ and carbon $|\sigma^C>$ nuclei which remain intact by Stark perturbation. Finally, the states of the CH$_3$F molecule subjected to an external electric field are

$$|\mu> \equiv |\beta, \xi> |\sigma^F> |\sigma^C>.$$ (10)

The manifold of these states will be denoted as the μ-basis. The Stark effect partially lifts the degeneracy of the α-states. But the μ-states remain degenerate in sign of M, and in quantum numbers σ, σ^F and σ^C.

IV. HYPERFINE LEVEL SPLITTING

In accordance with the general rules, the molecular Hamiltonian, $\hat{H}$, which contains now the hyperfine and Stark perturbations, can be expressed in the μ-representation as

$$\hat{H} = \sum_{\mu_1} \sum_{\mu_2} |\mu_2> < \mu_2|\hat{H}|\mu_1> < \mu_1| \equiv \hat{H}(o) + \hat{H}(p) + \hat{V},$$ (11)

5

where the sums run over the complete set of states. We recall that the operator $\sum |\mu><\mu|$ is the identity operator if the summation includes all states of the complete set. Eq.(11) shows how the molecular Hamiltonian can be split into three operators: $\hat{H}(o)$ and $\hat{H}(p)$ which have only diagonal matrix elements in the ortho and para subspaces, respectively, and operator $\hat{V}$, which has only matrix elements off-diagonal in the ortho and para quantum numbers.

When considering the combined level splitting by the three perturbations: Stark effect, hyperfine spin-rotation and spin-spin perturbations it is helpful to start with the Stark effect. Taking into account the Stark effect is not difficult because Stark perturbation does not mix the ortho and para states of a free molecule. In fact, transformation from the α-basis of a free molecule to the μ-basis gives the level splitting by the Stark effect.

A. Spin-rotation interaction

The next perturbation to be considered is the spin-rotation coupling which is due to the interaction of nuclear spins with the intramolecular magnetic field induced by molecular rotation. The spin-rotation interaction Hamiltonian is given by the operator [14,16]

$$\hbar \hat{H}_{SR} = -\sum_k \hat{\mathbf{I}}^{(k)} \bullet \mathbf{C}^{(k)} \bullet \hat{\mathbf{J}} \equiv \hbar \sum_k \hat{H}_{SR}^{(k)} , \qquad (12)$$

where $\hat{\mathbf{I}}^{(k)}$ and $\mathbf{C}^{(k)}$ are, respectively, the spin operator and the spin-rotation tensor for the k-th nucleus; $\hat{\mathbf{J}}$ is the molecular angular momentum operator and k denotes all nuclei in the molecule. The magnitude of the spin-rotation tensor $\mathbf{C}$ depends on the molecular spatial structure and motion of the molecular electrons [14].

Spin-rotation interaction is of the order $10 - 100$ kHz which is much smaller than the energy gaps between the states having different J and K ($> 10^2$ GHz), and is much smaller than the Stark splitting of states different in $|M|$ and ξ (> 10 MHz). Consequently, only matrix elements of $\hat{H}_{SR}$ diagonal in quantum numbers J, K, M, ξ and I are important for the calculation of the spin-rotation splitting of states [17]. Because the operator $\hat{H}_{SR}$ is a scalar, the only non-zero matrix elements will be the elements diagonal also in the spin projections σ, σ^F and σ^C. Explicit expressions for these matrix elements can be found in [16]. For example, the diagonal matrix elements for the spin-rotation interaction of the fluorine nucleus are

$$M\sigma^F \left[c_\alpha^F + \frac{K^2}{J(J+1)}(c_\beta^F - c_\alpha^F) \right] , \qquad (13)$$

where constants c_α^F and c_β^F are the diagonal elements of the tensor $\mathbf{C}^F$, calculated in the molecular system of coordinates. The spin-rotation tensor of fluorine and hydrogen nuclei are given in [16]. The tensor $\mathbf{C}^C$ for the carbon nucleus is absent in [16]. We will use for its estimation the relation: $\mathbf{C}^C = \mathbf{C}^F m^C / m^F$, where m^C and m^F are the magnetic moments of ^{13}C and F nuclei, respectively.

One can conclude, that the spin-rotation splitting of states appears to be rather simple in the μ-basis because this perturbation only shifts the states but does not mix them. As an example, the spin-rotation splitting of the state (J=9, K=3, M=9) is shown in Fig. 3b.

B. Spin-spin interaction

Nuclear spin-spin interaction in molecules is composed of dipole-dipole interaction of pairs of nuclei. The spin-spin interaction Hamiltonian for the two magnetic dipoles $\mathbf{m}_1$ and $\mathbf{m}_2$ separated by the distance r has the form [9]

$$
\begin{aligned}
\hbar \hat{H}_{12} &= P_{12} \hat{\mathbf{I}}^{(1)} \hat{\mathbf{I}}^{(2)} \vdots \mathbf{T}^{(12)} ; \\
T_{ij}^{(12)} &= \delta_{ij} - 3n_i n_j ; \quad P_{12} = m_1 m_2 / r^3 I^{(1)} I^{(2)} ,
\end{aligned} \tag{14}
$$

where $\hat{\mathbf{I}}^{(1)}$ and $\hat{\mathbf{I}}^{(2)}$ are the spin operators of the particles 1 and 2, respectively; $\mathbf{n}$ is the unit vector directed along $\mathbf{r}$; i and j are the Cartesian indices.

The total spin-spin interaction in $^{13}CH_3F$ ($\hat{H}_{SS}$) consists of the interactions between the three hydrogen nuclei ($\hat{H}_{HH}$), hydrogen - fluorine nuclei ($\hat{H}_{HF}$), hydrogen - carbon nuclei ($\hat{H}_{HC}$), and fluorine - carbon nuclei ($\hat{H}_{FC}$). Consequently, the total spin-spin Hamiltonian in $^{13}CH_3F$ is

$$
\hat{H}_{SS} = \hat{H}_{HH} + \hat{H}_{HF} + \hat{H}_{HC} + \hat{H}_{FC}. \tag{15}
$$

Explicit expressions for all these terms can be written on the basis of Eq.(14) for one pair of nuclei. For example, for the spin-spin interaction between the three hydrogen and fluorine nuclei one has

$$
\hbar \hat{H}_{HF} = P_{HF} \sum_n \hat{\mathbf{I}}^{(n)} \hat{\mathbf{I}}^F \vdots \mathbf{T}^{nF} ; \quad n = 1, 2, 3 . \tag{16}
$$

Here the sum runs over all hydrogen nuclei in the molecule. Complete definition of the spin-spin interaction requires knowledge of the dimensional factors P (see Eq.(14)) and the spatial structure of the molecule. These data can be found in Refs. [12,18].

Without hyperfine interactions, quantum states of the molecule subjected to an external electric field form the μ-basis. The intramolecular spin-spin perturbation $\hat{H}_{SS}$ has non-zero matrix elements diagonal and off-diagonal in quantum numbers J, K, M, σ, σ^F, and σ^C. The J, K-splitting of states is much larger than the spin-spin splitting which is on the order of $10 - 100$ kHz. Therefore, one can neglect the matrix elements of $\hat{H}_{SS}$ off-diagonal in J and K.

Under our conditions the Stark splitting of states different in $|M|$ is much larger than the spin-spin interaction. Thus, only the matrix elements of $\hat{H}_{SS}$ diagonal in M are important if $|M| > 1$ because of the selection rule $|\Delta M| \leq 2$ for the spin-spin interaction. Off-diagonal in M matrix elements of $\hat{H}_{SS}$ are important only for the states having $|M| = 1$. This particular case will be considered elsewhere. One can conclude, that the spin-spin perturbation of μ-states is determined by the matrix elements of $\hat{H}_{SS}$ diagonal in quantum numbers J, K, M, ξ, I and in the values of the sum $\sigma + \sigma^F + \sigma^C$.

To summarize, the hyperfine structure of molecular states in our case is determined by the hyperfine Hamiltonian $\hat{H}_{SR} + \hat{H}_{SS}$ spanned by the states different only in the projections of nuclear spins σ, σ^F, and σ^C. There are $4 \times 2 \times 2 = 16$ such states for ortho molecules:

$$| \beta_{ortho}, \xi > | \sigma^F > | \sigma^C >, \tag{17}$$

and $2 \times 2 \times 2 = 8$ states for para molecules:

$$| \beta_{para}\xi > | \sigma^F > | \sigma^C > . \tag{18}$$

Matrix elements of $\hat{H}_{SR}$ are give by Eq. (13). Calculation of the matrix elements of all terms of $\hat{H}_{SS}$ can be done in a way similar to that explained in the Appendix. After all necessary matrix elements of $\hat{H}_{SR}$ and $\hat{H}_{SS}$ are determined one can find the eigenstates and eigenvalues of the operator $\hat{H}_{SR} + \hat{H}_{SS}$. This will give the hyperfine level splitting of the molecular states under joint action of the spin-spin and spin-rotation interactions. In the case of ortho states one has to diagonalize the 16x16 matrix. For the para states one has to diagonalize the 8x8 matrix. Ortho and para quantum states of the molecule which take into account the Stark effect and both types of hyperfine interactions will be designated as the τ-basis. As an example, splitting of the ortho state $J=9$, $K=3$, $M=9$ by the spin-spin and spin-rotation interactions is shown in Fig. 3c. These calculations were done numerically. One can see from these data that the hyperfine interaction lifts completely degeneracy of the nuclear spin states.

V. CONVERSION SPECTRA

A. Rotational structure in the conversion spectra

For the calculation of the conversion spectra it is important to know the positions of ortho and para states in ^{13}CH$_3$F. The nuclear spin conversion in ^{13}CH$_3$F is dominated by mixing of the two level pairs: $(J=9, K=3)$–$(J'=11, K'=1)$ and $(20,3)$–$(21,1)$ [12,19]. Of these two level pairs the former has the smaller energy gap (130 MHz) and contributes nearly 65% to the conversion rate of a free molecule. The states $(11,1)$–$(9,3)$ are mixed by the spin-spin interaction only [12]. The spin-rotation interaction does not mix this pair of states because of the selection rule for the spin-rotation interaction $|\Delta J| \leq 1$ [20].

To describe the rotational structure in the conversion spectra [1] one has to include the Stark perturbation $\hat{V}_{St} = -\mathbf{d}\mathcal{E}$ into the $\hat{H}_0$ term of the splitting (1). As a result, an equation similar to Eq.(2) is obtained but in the μ-basis which accounts for the Stark effect. Note that the modeling of the off-diagonal elements of the collision integral (3) will also have the same form in the μ-basis. Further, one needs to know the matrix elements of the spin-spin perturbation which mixes ortho and para states of ^{13}CH$_3$F. From the total spin-spin perturbation (15) only the part, $\hat{V} = \hat{H}_{HH} + \hat{H}_{HF} + \hat{H}_{HC}$, produces the ortho-para state mixing. The matrix elements $V_{\mu'\mu}$ in the μ-basis can be calculated using the matrix elements of $\hat{V}$ in the α-basis [12] and the relation between these two bases given in Section III.

An overview of the rotational structure in conversion spectra of ^{13}CH$_3$F is shown in Fig. 4. The spectrum was calculated using $\Gamma = 1.75 \cdot 10^7$ s^{-1} which corresponds to the gas pressure 0.1 Torr. (Here and below we use the decoherence rate $1.75 \cdot 10^8$ s^{-1}/Torr [5]). For such a value of Γ the hyperfine structure of molecular states is not important because the

line broadening is much larger than the hyperfine splitting. At lower pressures the hyperfine level splitting does play an important role, as is shown in the next Section.

B. Hyperfine spectra

To calculate the hyperfine spectra of spin conversion one has to include both the Stark terms and the hyperfine terms into the operators $\hat{H}(o)$ and $\hat{H}(p)$ (see Eq.(11)). This will result in transformation of the μ-basis of molecular states to the τ-basis. Matrix elements of the perturbation $\hat{V}$ between ortho and para states should be calculated in the τ-basis also. The calculations were done by using the matrix elements of $\hat{V}$ in the α-basis from [12] and the matrix which transforms the α-basis to the τ-basis.

The new expression for the conversion rate obtained in this way, which is exactly Eq.(2) with τ indices instead of α indices, needs further modification. The point is that hyperfine structure in the spin conversion spectra can be revealed only at rather low pressures. The gas pressure should be low enough to make the decoherence rate Γ smaller than the hyperfine splitting. The latter is estimated to be of the order of V. Consequently, the condition $\Gamma \lesssim V$ should be fulfilled.

As was shown in [8], calculation of the spin conversion rate in first order perturbation theory is not valid if $\Gamma \lesssim V$. This is a consequence of the level population saturation by intramolecular ortho-para states mixing. The saturation effect can be accounted for by using the new expression for the conversion rate

$$\gamma = \sum_{\tau' \in p, \tau \in o} \frac{2\Gamma_{\tau'\tau}|V_{\tau'\tau}|^2}{\Gamma_{\tau'\tau}^2 + \omega_{\tau'\tau}^2 + 4\frac{\Gamma_{\tau'\tau}}{\nu}|V_{\tau'\tau}|^2} \left(W_{\tau'} + W_{\tau}\right), \tag{19}$$

where ν is the rotational relaxation rate which was assumed equal for ortho and para isomers. Expression (19) is a straightforward generalization of the result [8], where the theory was developed for the mixing of only one pair of ortho and para states.

As is clear from Eq. (19), the saturation effect is most important for "strong resonances", which have large values of the mixing matrix elements $V_{\tau'\tau}$. As an example of the saturation effect at work, we show the hyperfine structure of the strongest peak in the spectrum of Fig. 4 which results from the crossing of magnetic sublevels $M'=11$ and $M=9$. This hyperfine spectrum is given in Fig. 5. Calculation of the spectrum was performed for the gas pressure 0.1 mTorr, and the ratio $\Gamma/\nu = 10$. From the spectrum of Fig. 5 one concludes that the saturation effect can produce substantial broadening of the spectral lines. Consequently, the hyperfine structure in Fig. 5 remains unresolved. Decreasing the gas pressure does not result in a decrease in the width of the lines.

Nevertheless, well-resolved hyperfine spectra of spin conversion can be obtained if one chooses "weak resonances" having small magnitude of $V_{\tau'\tau}$. As an example, the hyperfine structure produced by the "weak crossing" of the $M'=7$ and $M=9$ states is shown in Fig. 6. One can see that in this case the hyperfine structure is well resolved. Decreasing the gas pressure makes the lines even more narrow.

It is interesting to understand the accuracy of the simplified approach to the conversion spectra in which hyperfine splitting of molecular states is not taken into account. In Fig. 7 we show the pressure dependence of the amplitude of the "strong resonance" (9,3,9)–(11,1,11) calculated using the simplified and the present model. One can see that a 10% difference in the two amplitudes already appears at 5 mTorr. At the pressure 1 mTorr, the present model gives one-third the value of the old model.

VI. CONCLUSIONS

A theoretical model of hyperfine spectra of nuclear spin conversion has been developed. Calculations have been performed for the conversion of spin isomers of $^{13}CH_3F$ molecules subjected to an external electric field. The spin-rotation and the spin-spin intramolecular interactions were taken into account in the calculations.

It has been shown that the hyperfine structure of spin conversion spectra can be substantially distorted by the saturation effect. In the case of "strong resonances" this effect hides the hyperfine structure of the spectra completely. It had been proposed to observe the hyperfine spectra by using "weak resonances" which have small ortho-para matrix elements. Such weak resonances have been found for the $^{13}CH_3F$ molecules and hyperfine spectra for them have been calculated.

Calculations performed in the present paper have revealed the conditions at which experimental observation of the hyperfine spectra of nuclear spin conversion can be performed. These conditions include the choice of suitable level crossings and gas pressure. The pressure at which the hyperfine structure of the spectra is resolved appeared to be rather low. This implies strong limitations to the experimental setup, viz., molecular collisions with the walls should contribute to the decoherence rate Γ not much more than collisions in the bulk. The latter should be on the order of 10^4 s^{-1} only.

The theoretical model proposed in this paper is rather general. It can be applied to molecules having various symmetries without changing its essence. Another possible extension of the model can be related to the use of the Zeeman effect for the level splitting instead of the Stark effect considered in the paper.

VII. ACKNOWLEDGMENT

VIII. APPENDIX

As an example, we give here the calculation of the matrix elements of $\hat{H}_{HF}$. First, let us express the $\hat{H}_{HF}$ through the spherical tensors [9]:

$$\hat{H}_{HF} \quad \equiv \quad \sum_n \hat{H}_{HF}^{(n)} \quad = \quad P_{HF} \sum_n \sum_{q_1, q_2, q} (-1)^q < 1, q_1, 1, q_2, |2, -q> \hat{I}_{1,q_1}^{(n)} \hat{I}_{1,q_2}^F T_{2q}^{nF}. \qquad (20)$$

Here $\hat{H}_{HF}^{(n)}$ is the spin-spin operator of the interaction between fluorine and the n-th hydrogen nuclei; $n = 1, 2, 3$ denotes the hydrogen nuclei; $< \ldots | \ldots >$ stands for the Clebsch-Gordan coefficient.

Calculations of the matrix elements of $\hat{H}_{HF}$ can be substantially simplified if one takes into account that the matrix elements $< \mu_1 | \hat{H}_{HF}^{(n)} | \mu_2 >$ are equal for all n. This can be proven by applying to these matrix elements the cyclic permutation, P_{123}, of the three equivalent protons. Taking this simplification into account one has

$$< \mu_1 | \hat{H}_{HF} | \mu_2 > \quad = \quad 3 < \mu_1 | \hat{H}_{HF}^{(1)} | \mu_2 > . \qquad (21)$$

The matrix elements of the operator $\hat{H}_{HF}$ which contribute to the spin-spin level splitting (see Section IV) are given by the expression

$$< \mu_2 | H_{HF} | \mu_1 > \quad = \quad 3 P_{HF} \sum_q < 1, q, 1, -q | 2, 0 > < I, \sigma_2, K | \hat{I}_{1,-q}^{(1)} | I, \sigma_1, K > \times$$
$$< \sigma_2^F | \hat{I}_{1,q}^F | \sigma_1^F > < J, K, M | T_{2,0}^{1F} | J, K, M > \delta_{\sigma_2^C, \sigma_1^C}. \qquad (22)$$

The matrix elements in Eq.(22) can be evaluated using the following relations. The matrix elements of the spatial tensor $T_{2,0}^{1F}$ are given in Ref. [9]. In our particular case one has

$$< J, K, M | T_{2,0}^{1F} | J, K, M > \quad = \quad < J, K, 2, 0 | J, K > < J, M, 2, 0 | J, M > \mathcal{T}_{2,0}^{1F}, \qquad (23)$$

where $\mathcal{T}_{2,0}^{1F}$ is the spherical tensor component of $\mathbf{T}^{1F}$ calculated in the molecular frame. Finally, the matrix elements of the spin operators $\hat{I}_{1,-q}^{(1)}$ and $\hat{I}_{1,q}^F$ can be evaluated using the Wigner-Eckart theorem which states for the spherical tensor of rank κ [9]:

$$< J', M' | f_{\kappa,q} | J, M > \quad = \quad i^\kappa (-1)^{J_{max} - M'} \begin{pmatrix} J' & \kappa & J \\ -M' & q & M \end{pmatrix} < J' || f_\kappa || J >, \qquad (24)$$

where $(: : :)$ stands for a 3j-symbol and $< J' || f_\kappa || J >$ is the reduced matrix element. Eqs.(22)-(24) allow us to perform the calculations of the matrix elements of $\hat{H}_{HF}$.

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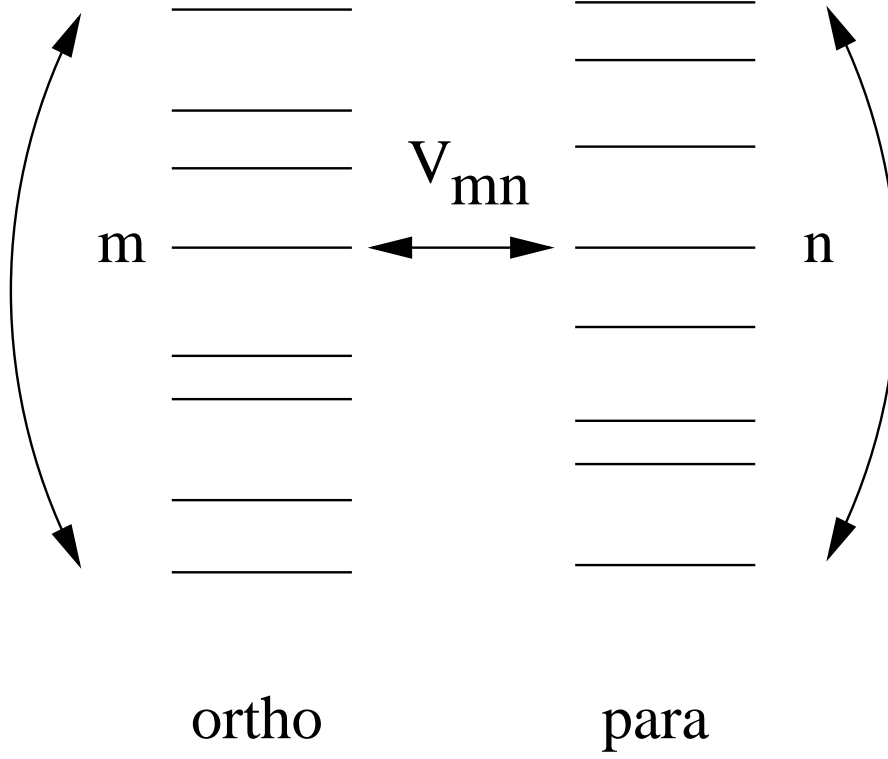[20] K. I. Gus'kov, Zh. Eksp. Teor. Fiz. **107**, 704 (1995), [JETP. **80**, 400-414 (1995)].

FIG. 1. *Schematic of the ortho and para states of the CH_3F molecule. It is assumed that only one pair of ortho and para states $(m - n)$ is mixed by an intramolecular perturbation $\hat{V}$. The bent lines indicate transitions induced by collisions with gas particles. These collisions do not produce direct transitions between molecular ortho and para states.*
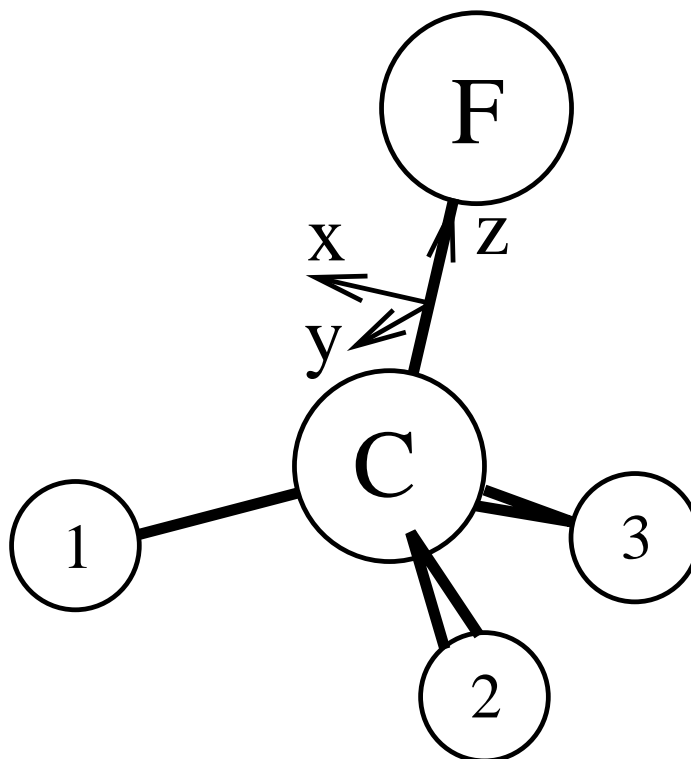
FIG. 2.   *Orientation of the molecular system of coordinates. It has its origin in the molecular centre of mass and is oriented by the numbered hydrogen nuclei in such a way that the xy plane is parallel to the hydrogen plane, the x axis is directed to the H^1 atom and the y axis is between the H^1 and H^2 atoms. The z axis is directed along the molecular symmetry axis.*
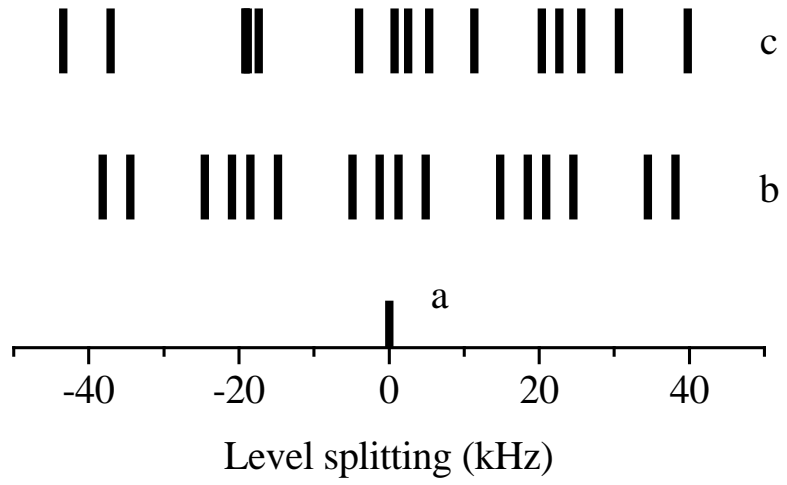
FIG. 3. *Splitting of the state $J=9$, $K=3$, $M=9$ of $^{13}CH_3F$: (a) no hyperfine perturbation; (b) splitting under the spin-rotation perturbation; (c) splitting by joint action of the spin-rotation and spin-spin perturbations. Note that three components near 19 kHz are accidentally nearly degenerate.*
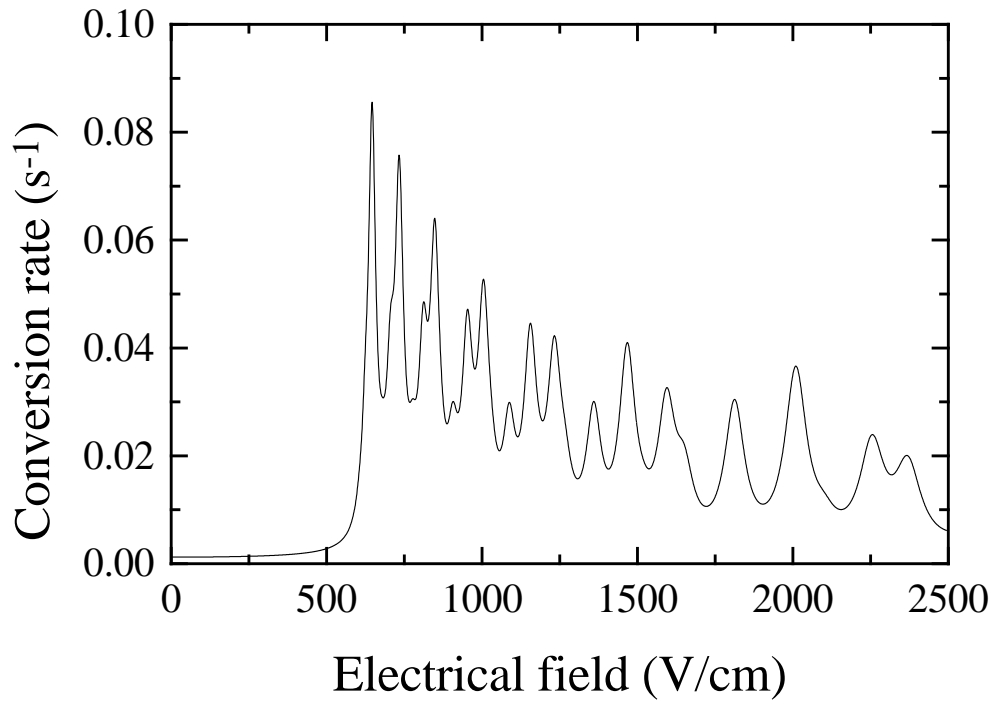
FIG. 4.   *Overview of the level-crossing resonances in the conversion (conversion spectra) of $^{13}CH_3F$ nuclear spin isomers. The decoherence rate in this example was taken equal $\Gamma = 1.75 \cdot 10^7\ s^{-1}$ (gas pressure 0.1 Torr).*
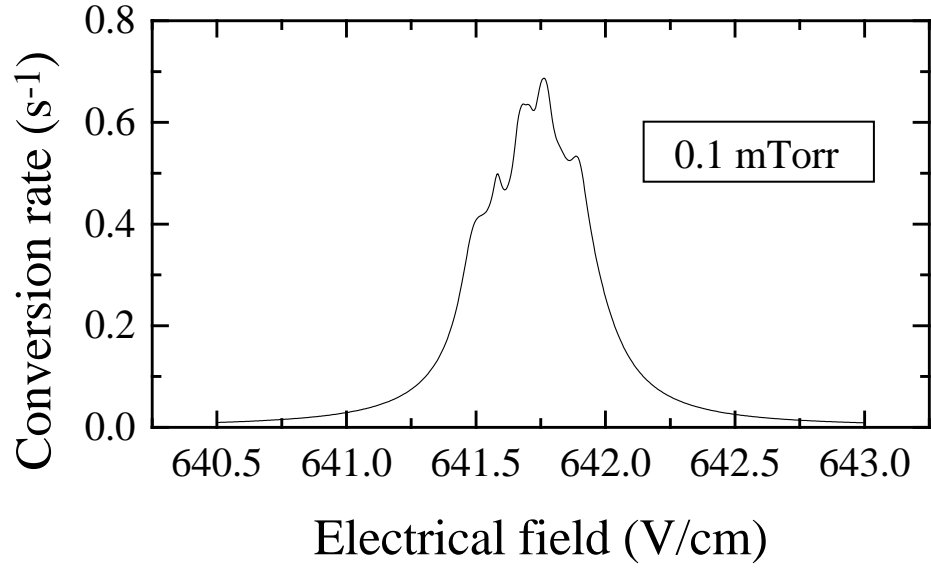
FIG. 5. *Hyperfine structure of the "strong resonance" resulting from the crossing of magnetic sublevels M'=11 and M=9. The gas pressure is 0.1 mTorr.*
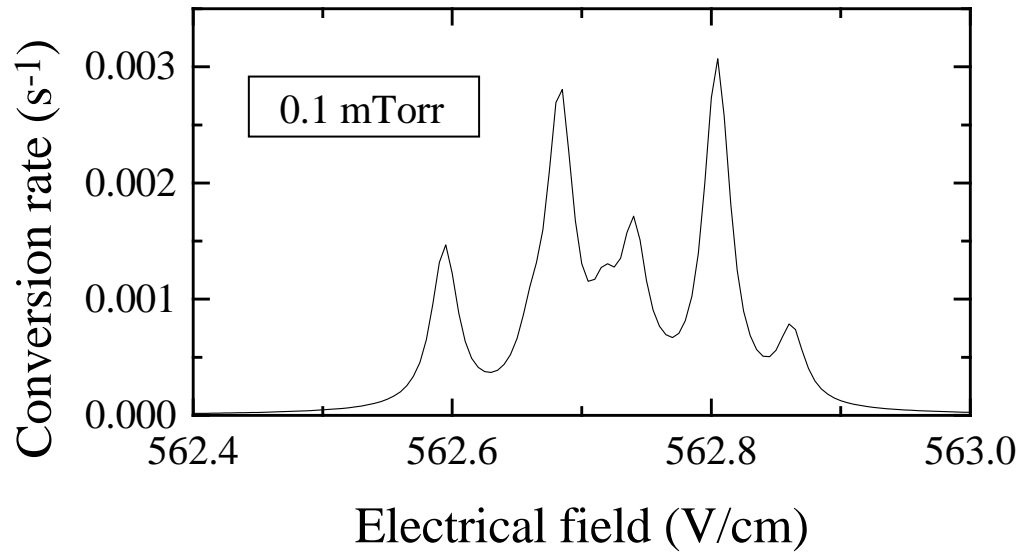
FIG. 6. *Hyperfine structure of the "weak resonance" resulting from the crossing of magnetic sublevels $M'=7$ and $M=9$. The gas pressure is 0.1 mTorr.*
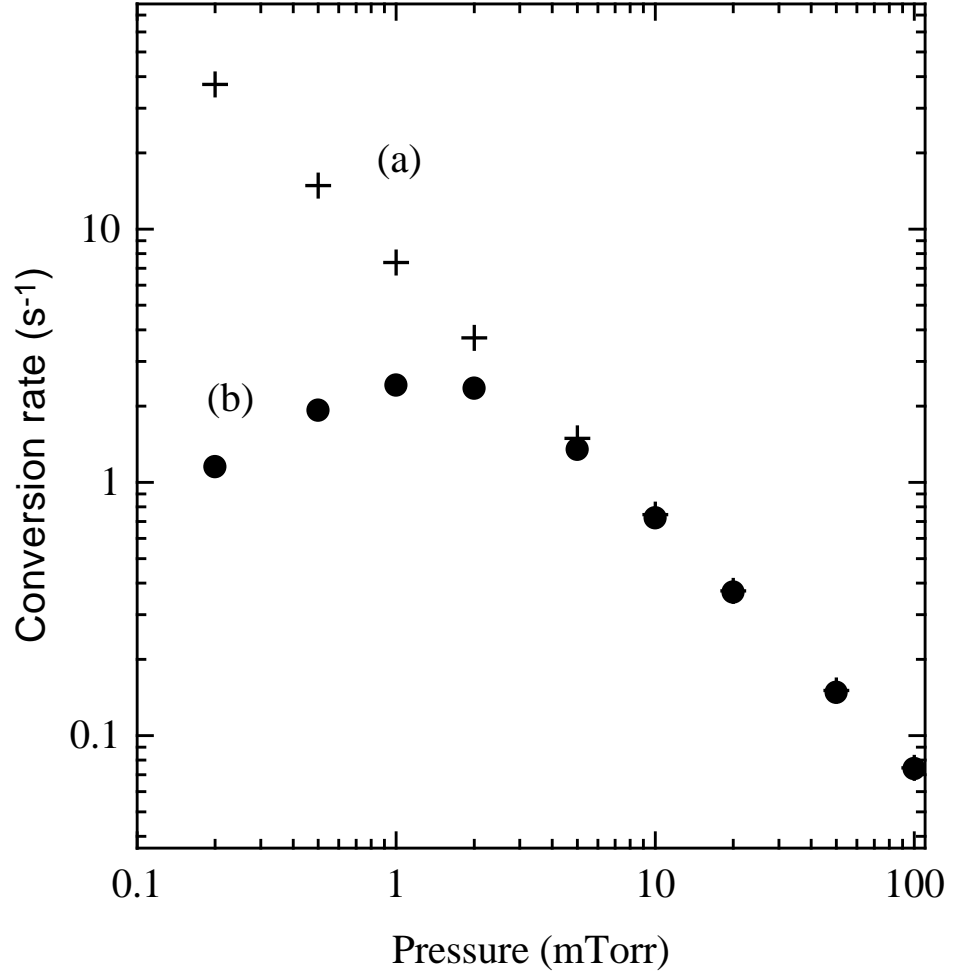
FIG. 7. *Pressure dependence of the amplitude of the "strong resonance" (9,3,9)–(11,1,11) (a) without and (b) with accounting of the hyperfine splitting of molecular states.*